Angular Substituents via Cyclopropane Derivatives of β, γ-Unsaturated Ketones[1]

JAMES J. SIMS AND V. K. HONWAD

Department of Plant Pathology, University of California, Riverside, California 92502

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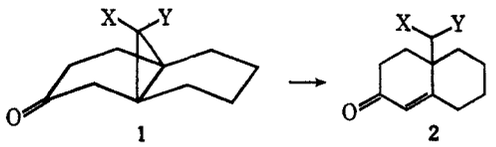
A method for introducing angular substituents in fused-ring systems is described. The base-catalyzed ring opening of β,γ-cyclopropyl ketones is facilitated by the presence of electron-withdrawing groups on the cyclopropane ring. The required cyclopropanes may be synthesized through the use of substituted carbenes. Substituents X and Y which promote ring opening of compound **1** are the following: X = CO_2CH_3, Y = H; X = Y = Cl; X = Y = Br. For the compound X = Cl, Y = H, no ring opening is observed. The reaction of chlorocarbene, generated from methyllithium and methylene chloride, with the Birch reduction products of naphthalene and tetralin is described.

We have been interested in ring-opening reactions of cyclopropane compounds as a method of introducing methyl groups into alicyclic molecules, especially at angular positions.[2,3] The introduction of such methyl groups is a customary hurdle in the synthesis of terpenes and steroids. Many of these syntheses hinge upon the proper introduction of a methyl group.[4] Angular substituents other than methyl groups also occur in terpenoids; thus we were interested in ring opening of

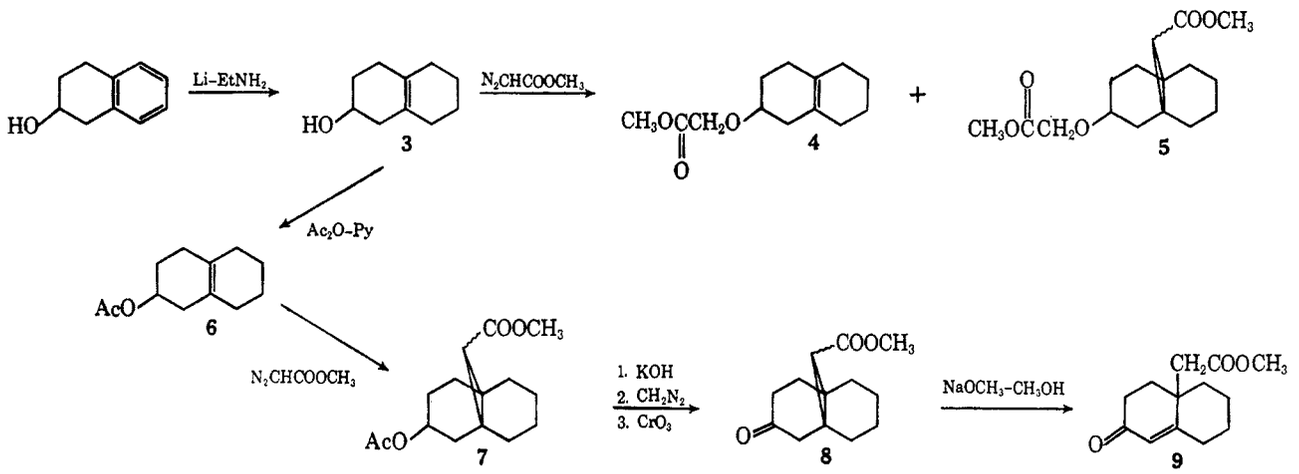


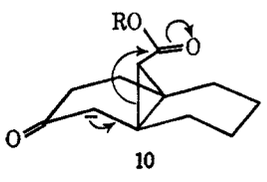
substituted cyclopropanes as a method of introducing other substituents (*e.g.*, **1** → **2**).

One can imagine a number of possible substituents X and Y which could be introduced by a sequence starting from an olefin and a substituted carbene. We were interested in how various substituents would affect the ring opening of the ketones **1**, since when X and Y are hydrogen, aldol condensation is faster than ring opening base catalysis.[2] It would be expected that substituents that could stabilize a negative charge on the carbon bearing X and Y would also accelerate base-catalyzed ring opening. Base-catalyzed opening of cyclopropyl ketones is preferred to acid-catalyzed opening because the former gives ring opening in one direction,[2,5] while the latter may give opening in two directions.[2]

The first substituted cyclopropane we examined was the tricyclic keto ester, **8**, prepared as shown in Scheme I. The catalyzed decomposition of methyl diazoacetate with **3** led to ethers **4** and **5** which were of no value to this study. Protection of the alcohol as an acetate (**6**) before reaction with methyl diazoacetate led to the desired ester **7** in low yield. The tetrahydropyranyl ether of **3** was also studied as was ethyl diazoacetate in attempts to increase the yield of the cyclopropane but no significant increase was obtained. The major products of all these reactions were maleic and fumaric acid esters. Once obtained, the keto ester **8** proved to undergo base-catalyzed ring opening with remarkable ease. We feel that the ester carbonyl probably acts as an electron sink as indicated in **10**.

SCHEME I





Unfortunately while the ring opening is a good reaction, some way to increase the yield of the cyclopropane

(1) This research has been supported by Public Health Service Grant AM 10474 from the National Institute of Arthritis and Metabolic Diseases.

(2) J. J. Sims, *J. Org. Chem.*, **32**, 1751 (1967).

(3) J. J. Sims, *J. Am. Chem. Soc.*, **87**, 3511 (1965).

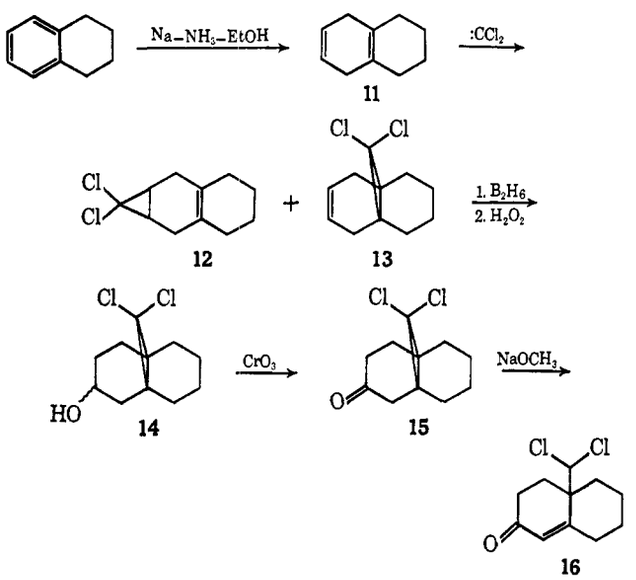
(4) L. Velluz, J. Valls, and G. Nomine, *Angew. Chem.*, **77**, 185 (1965); G. Stork, *Pure Appl. Chem.*, **9**, 131 (1964).

(5) R. Ginsig and A. D. Cross, *J. Am. Chem. Soc.*, **87**, 4629 (1965).

products in the diazo ester decomposition must be found before the sequence 3 → 9 can be of significant synthetic value.

We next turned to another carbene reaction in order to prepare a dichlorocyclopropane. The acetate **4** did not react to any appreciable extent with dichlorobarbene generated from $CHCl_3$–KO-*t*-Bu so a different approach was used as outlined in Scheme II. Hydrocarbon **11**

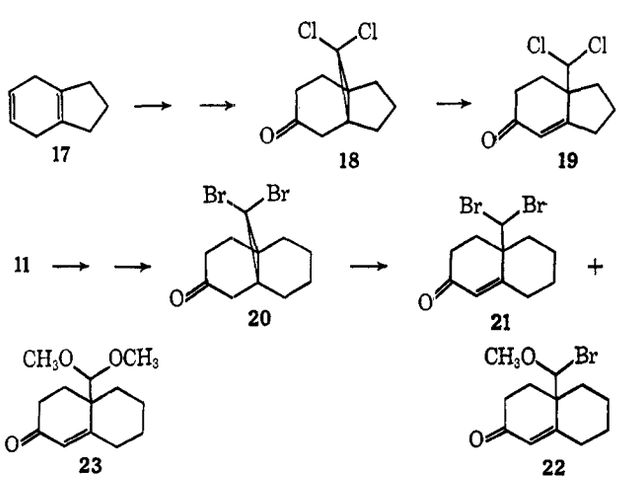
Scheme II



was smoothly converted by the action of $CHCl_3$–KO-*t*-Bu into a mixture of monoadducts **12** (20%) and **13** (80%). Separation was accomplished by a hydroboration–oxidation sequence to give ketone **15.** Treatment of **15** with sodium methoxide in methanol gave rise to the ketone **16** in 79% yield. Longer refluxing did not cause displacement of chloride.

A similar sequence (Scheme III) was carried out with

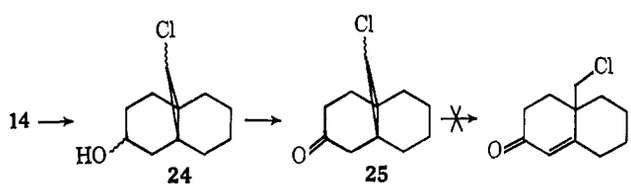
Scheme III



1,4-dihydroindane (**17**) leading to ketone **18** which underwent smooth ring opening to give **19.** Hydrocarbon **11** was also converted with dibromocarbene to ketone **20** which did not give a clean reaction such as **15** and **18.** Mild conditions, 1-hr reflux and sodium methoxide in methanol, gave a mixture of **21** and **22** which were only difficultly separable. Longer reflux of **20** or **21** with sodium methoxide in methanol did not cause any further displacement of bromide to produce the ketoacetal **23**; perhaps the first bromide was displaced in the ring-opening process. The progress of the ring-opening reaction of **20** could be followed by watching the disappearance of the saturated carbonyl peak and the corresponding appearance of the unsaturated carbonyl peak in the infrared spectra of the reaction mixture. Upon long reflux and complete disappearance of the C=O peak of **20** a new saturated carbonyl peak 5.85 μ appeared and grew to a constant size relative to the unsaturated peak. We have not yet been able to separate the compound(s) responsible for this new peak. The mixture after long reflux contains at least four compounds as shown in tlc.

Since the dihalocycloprpane ketones underwent ring opening so readily we decided to investigate the reactivity of monohalocyclopropane ketones. The preparation of ketone **25,** shown in Scheme IV, pro-

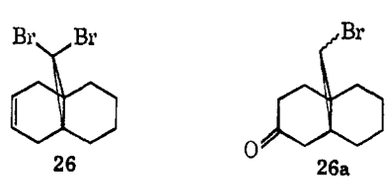
Scheme IV



ceeded from **14** by reduction with tributyltin hydride[6] to the monochloro alcohol **24.** Jones oxidation of **24** gave the chloro ketone **25.** The problem with this sequence was that both **24** and **25** distilled at a similar enough temperature as the tributyltin chloride that they could not be separated by distillation.

Separation, in low yield, was accomplished by preparation of the semicarbazone of **25** as a crystalline derivative followed by regeneration of the ketone with pyruvic and acetic acids. The monohalocyclopropyl ketone **24** proved to be much less reactive in the ring-opening reaction; no appreciable ring opening took place even after 20 hr of reflux with sodium methoxide in methanol. The solution turned dark and only starting material could be isolated.

Several other methods have been reported to reduce dihalocyclopropanes to monohalocyclopropanes; these include the sodium salt of dimethyl sulfoxide,[7] chromous sulfate,[8] and methylmagnesium bromide.[9] We had no success with any of these reagents, with either **14** or the



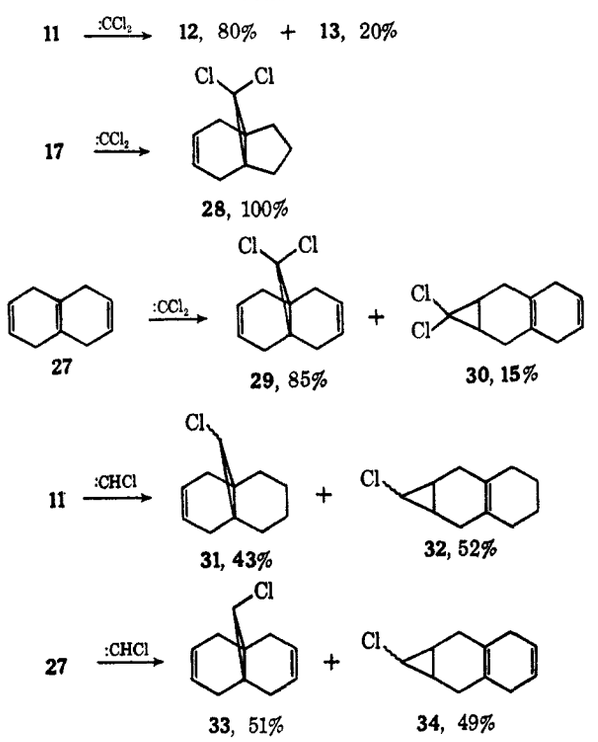
dibromocyclopropane **26.** Thus we did not prepare ketone **26a** to check its ring-opening tendency.

(6) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28,** 703 (1963).
(7) C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Cardenas, and P. D. Gardener, *Chem. Ind.* (London), 766 (1965).
(8) H. Nozaki, T. Aratani and R. Noyori, *Tetrahedron*, **23,** 3645 (1967); C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **88,** 4447 (1966).
(9) D. Seyferth and B. Prokai, *J. Org. Chem.*, **31,** 1702 (1966).

Direct preparation of the needed monohalocyclopropanes was not possible since the monohalocarbene from methyllithium and methylene chloride showed less selectivity than dichlorocarbene did when allowed to react with isotetralin or **11**; significant addition of monochlorocarbene took place at the disubstituted double bonds. This latter result is not too surprising as monochlorocarbene seems to be less selective than dichlorocarbene.[10]

A comparison of the products formed by the reaction of dichlorocarbene and monochlorocarbene with the previously mentioned olefins is presented in Scheme V.

SCHEME V



It is apparent from these data that the tetrasubstituted double bond of olefin **11** is less reactive than that of **17** or **27**. The selectivity looks even greater when one remembers that in **27** there are two disubstituted double bonds to compete with the central double bond. The trend is still apparent even with the less selective monochlorocarbene.[10] The reason for this selectivity is presumably a steric one, in which hydrogens in the saturated ring of **11** may interfere with reaction at the central double bond. The familiar *exo* attack of the norbornene double bond by most electrophilic reagents is a similar situation. Neither **27** nor **17** have hydrogens which can interfere greatly with the central double bond.

Experimental Section[11]

Preparation of Acetoxy Ester 7.—The alcohols, 1,2,3,4-tetrahydro-2-naphthol and **3**, were prepared by previously described methods.[2,12] The acetate **6** was prepared by treatment of **3** with acetic anhydride–pyridine.

To a stirred mixture of 1.4 g of **6** and 100 mg of anhydrous $CuSO_4$ under N_2 was added slowly 4 g of methyl diazoacetate. The reaction was exothermic and N_2 evolution was observed. After 2 hr at room temperature the mixture was diluted with CH_2Cl_2, filtered, concentrated, and distilled (140°, 0.1 mm) to remove dimethyl fumarate, dimethyl maleate, and starting material. The undistilled residue was distilled in a kugelrohr (100°, 0.1 mm) to yield 600 mg of a dark brown liquid. Chromatography on alumina gave 180 mg of **7**: infrared ($CHCl_3$), 1739 cm^{-1} (ester and acetate C=O); nmr (CCl_4), τ 8.15 (3 H singlet, $OCOCH_3$), 6.4 (3 H singlet, CO_2CH_3), 5.18 (1 H, HCO). *Anal.* Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 68.17; H, 8.58.

Preparation of Keto Ester 8.—Saponification of 800 mg of **7** was carried out overnight at room temperature in methanolic KOH. The crude acid so obtained was esterified with diazomethane and immediately oxidized with Jones reagent.[13] The oxidation product was distilled in a kugelrohr (115°, 0.1 mm) to give 225 mg (33%) of **8**: infrared ($CHCl_3$), 1721 cm^{-1} (ester and ketone C=O); nmr (CCl_4), τ 6.38 (3 H singlet, CO_2CH_3). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.47; H, 8.34.

Preparation of Unsaturated Ketone 9.—Ketone **8** (165 mg) dissolved in 3 ml of dry methanol was added under N_2 to a cold solution of 100 mg of $NaOCH_3$ in 3 ml of dry methanol. The mixture was warmed to 40° for 4 hr then cooled, diluted with water, and extracted with ether. The ether extract was dried ($MgSO_4$) and evaporated under vacuum. Chromatography on alumina gave 20 mg of starting material and 40 mg (32%) of ketone **9**: infrared ($CHCl_3$), 1667 (conjugated C=O), 1724 (ester C=O), 1613 cm^{-1} (C=C); nmr (CCl_4), τ 6.33 (3 H singlet, CO_2CH_3), 4.32 (1 H broad C=CHC=O); ultraviolet, λ_{max}^{MeOH} 237 mμ (ϵ 11,400). This compound was very unstable; no satisfactory analysis was obtained.

Preparation of Dichlorocyclopropyl Compounds 12 and 13.—Olefin **11**[14] (11 g), 30 ml of benzene, and 15.5 g of KO-*t*-Bu were placed in a 250-ml, three-neck flask fitted with a stirrer, dropping funnel, and N_2 inlet. The flask was cooled in an ice bath while 11 g of $CHCl_3$ was added slowly with efficient stirring. After the addition was complete the mixture was stirred for 2 hr at room temperature then quenched with 100 ml of water. The ether extract of the mixture was dried ($MgSO_4$), concentrated, and distilled yielding two fractions. The first fraction (55–59° (2 mm) was starting material, while the second, 7.8 g (105–107°, 2 mm), was a 20:80 mixture of **12** and **13** as shown by vpc analysis.[15]

Preparation of Alcohol 14.—The preceding mixture of **12** and **13** (10.8 g), 40 ml of dry tetrahydrofuran (THF), and 1.0 g of finely powdered $NaBH_4$ were placed in a flask and stirred while a solution of 4 ml of dry THF containing 4.0 g of freshly distilled $BF_3 \cdot Et_2O$ was slowly added. After 1 hr at room temperature the reaction mixture was oxidized by adding 15 ml of 3 *N* NaOH followed by 15 ml of 30% H_2O_2. The ether extract of the mixture was washed with saturated NaCl, dried ($MgSO_4$), and concentrated. Distillation gave 2 g of **12** (90–95°, 0.5 mm) and 7.0 g of **14** (112–115°, 0.5 mm), which solidified. After recrystallization from ether, **14** had mp 83–85°. *Anal.* Calcd for $C_{11}H_{16}OCl_2$: C, 56.18; H, 6.85; Cl, 30.15. Found: C, 56.20; H, 6.78; Cl 29.75.

Preparation of Ketone 15.—The alcohol **14** (7 g) was oxidized by Jones reagent[13] yielding after recrystallization from ether 4.0 g of **15**: mp 73–75°; infrared ($CHCl_3$), 1709 cm^{-1} (C=O). *Anal.* Calcd for $C_{11}H_{14}OCl_2$: C, 56.58; H, 6.04; Cl, 30.51. Found: C, 56.26; H, 6.03; Cl, 30.90.

The semicarbazone had mp 222–226° dec.

Preparation of Ketone 16.—Ketone **15** (430 mg), 10 ml of dry methanol, and 200 mg of anhydrous $NaOCH_3$ was refluxed for 4 hr under N_2. The mixture was cooled, diluted with water, and extracted with ether. The ether extract was washed with

(10) W. Kirmse "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 190.

(11) Analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N. Y., and Elek Microanalytical Laboratories, Torrance, Calif. Infrared spectra were determined with a Perkin-Elmer Model 137 Infracord. Ultraviolet spectra were determined with a Perkin-Elmer Model 202. The nmr spectra were recorded with a Varian Model A-60. Chemical shifts are expressed as τ values relative to tetramethylsilane as an internal standard.

(12) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

(13) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedone, *J. Chem. Soc.*, 39 (1946).

(14) Prepared by Birch reduction of tetralin; *cf.* H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Non-aqueous Solvents," Vol. 1, Part 2, John Wiley and Sons, Inc., New York, N. Y., 1963.

(15) A 15% butanediol succinate on Chromosorb W column was used.

saturated NaCl, dried ($MgSO_4$), and concentrated to give a solid. Recrystallization from ether gave 340 mg (79%) of ketone **16**: infrared ($CHCl_3$), 1667 (conjugated C=O), 1621 cm^{-1} (C=C); nmr ($CDCl_3$), τ 3.98 (1 H, C=CHC=O), 3.52 (1 H, $HCCl_2$); ultraviolet, λ_{max}^{MeOH} 237 mμ (ε 12,900). *Anal.* Calcd for $C_{11}H_{14}OCl_2$: C, 56.58; H, 6.04; Cl, 30.51. Found: C, 56.45; H, 6.17; Cl, 30.73.

Preparation of Ketone 18.—The reaction of olefin **17**[16] with dichlorocarbene (as above) gave a single monoadduct **28**, which was identical with an authentic sample.[17] The adduct **28** (9 g) was subjected to hydroboration as described earlier yielding 5 g of a crystalline alcohol, mp 111–112°. *Anal.* Calcd for $C_{10}H_{14}OCl_2$: C, 54.33; H, 6.39; Cl, 31.45. Found: C, 54.34; H, 6.39; Cl, 31.45.

Oxidation of the above alcohol (4 g) with Jones reagent[13] gave 3 g of ketone **18**: mp 58–59°; infrared ($CHCl_3$), 1718 cm^{-1} (C=O). *Anal.* Calcd for $C_{10}H_{12}OCl_2$: C, 54.81; H, 5.52; Cl, 32.36. Found: C, 54.78; H, 5.44; Cl, 32.10.

Preparation of Unsaturated Ketone 19.—Ketone **18** (1.2 g) in 10 ml of dry methanol was added to 3 ml of dry methanol containing 325 mg of $NaOCH_3$. After 8 hr of reflux the reaction mixture was diluted with water and extracted with ether. The ether solution was dried ($MgSO_4$), concentrated, and distilled to give 400 mg of ketone **19**: bp 95–98° (0.1 mm); infrared ($CHCl_3$), 1667 cm^{-1} (conjugated C=O); ultraviolet, λ_{max}^{MeOH} 228 mμ (ε 7115); nmr ($CDCl_3$), τ 3.91 (1 H, $HCCl_2$), 4.12 (1 H, C=CHC=O). A satisfactory microanalysis could not be obtained from this ketone due to its unstable nature. Samples kept at −15° under nitrogen rapidly turned dark.

Preparation of Dibromo Ketone 20.—The dibromocarbene addition to olefin **11**[14] was carried out in the same manner as described for the preparation of **12** and **13**, with the exception that bromoform was substituted for chloroform. The monoadducts obtained contained 80% of **25**. The mixture of monoadducts (22 g) was carried through the previously described hydroboration–oxidation sequence to give a crude product which partially decomposed on attempted distillation. Thus the crude product was oxidized with Jones reagent[13] to yield after work-up a semisolid residue from which 7 g of the desired ketone could be separated; mp 84–86°; infrared ($CHCl_3$), 1709 cm^{-1} (C=O). *Anal.* Calcd for $C_{11}H_{14}OBr_2$: C, 41.32; H, 4.38. Found: C, 41.56; H, 4.49.

Treatment of Ketone 20 with Sodium Methoxide.—A solution containing 5 g of ketone **20** and 500 mg of $NaOCH_3$ in 30 ml of dry methanol was refluxed under N_2 for 1 hr. Work-up as previously described gave 3.5 g of a mixture of **21** and **22**. Careful chromatography over silicic acid, eluting with $CHCl_3$, gave fractions from which ketones **21** and **22** could be isolated. First eluted was **21**: infrared ($CHCl_3$), 1664 (conjugated C=O), 1613 cm^{-1} (C=C); nmr ($CDCl_3$), τ 4.28 (1 H, C=CHC=O), 3.90 (1 H, $HCBr_2$); ultraviolet, λ_{max}^{MeOH} 239 mμ (ε 12,880); semicarbazone mp 210–212° dec. *Anal.* Calcd for $C_{12}H_{17}ON_3Br_2$: C, 38.03; H, 4.51. Found: C, 38.20; H, 4.82.

The ketone **22** was eluted second: mp 129–30°; infrared, 1664 cm^{-1} (conjugated C=O); nmr ($CDCl_3$), τ 6.70 (3 H, OCH_3), 4.23 (1 H, C=CHC=O), 5.39 (1 H, $HC(Br)OCH_3$); ultraviolet, λ_{max}^{MeOH} 225 mμ (ε 3619) 254 mμ (ε 6000). *Anal.* Calcd for $C_{12}H_{17}O_2Br$: C, 52.76: H, 6.27. Found: C, 52.95; H, 6.45.

Preparation of Chloro Ketone 25.—To a stirred solution of 14 g of alcohol **14** in 15 ml of dry ether, under N_2, was added 17 g of tributyltin hydride.[6] The ether was distilled off; the mixture was heated for 7 hr at 90° and then distilled under vacuum. The products of the reaction codistilled so the total reaction mixture was oxidized with Jones reagent.[13] Again distillation could not effect separation. The mixture was then treated with semicarbazide hydrochloride and sodium acetate in methanol. After standing for a few hours at room temperature the crude semicarbazone of **25** separated and was recrystallized from methanol; yield 5.3 g, mp 184–186°.

(16) E. Giovannini and H. Wegmüller, *Helv. Chim. Acta*, **41**, 933 (1958).

(17) P. C. Radlick and W. M. Rosen, University of California at Riverside, Riverside, personal communication, 1968.

The semicarbazone (3 g), pyruvic acid (3 g), 26 ml of acetic acid, and 3 ml of H_2O were stirred at room temperature for 17 hr. The reaction mixture was neutralized with saturated $NaHCO_3$ and extracted with ether. The ether solution was dried ($MgSO_4$), concentrated, and distilled to yield 1.5 g of ketone **25**, bp 89–91° (3 mm). A semicarbazone prepared from this material had mp 186–188°. *Anal.* for $C_{12}H_{18}OClN_3$: C, 56.36; H, 7.09. Found: C, 56.47; H, 7.12.

Reaction of 25 with Sodium Methoxide.—Dry sodium methoxide (120 mg) and ketone **25** (500 mg) were dissolved in 5 ml of methanol and refluxed for 20 hr under N_2. No ring opening took place under these conditions as shown by the infrared spectrum of the product.

Reaction of Olefin 11 with CH_3Li and CH_2Cl_2.—Following the described procedure,[18] 13.5 g of olefin **11** and 9 g of CH_2Cl_2 was treated with 50 ml of 4.6% CH_3Li. Distillation of the product gave 7.0 g (120–130°, 25 mm) of a mixture of monoadducts. Analysis by vapor phase chromatography (10% Carbowax on Chromosorb P, 200°) showed that four compounds were present in this fraction. The nmr spectrum of the fraction contained two triplets [τ 6.88 (J = 8.0 Hz), 7.31 (J = 3.0 Hz)] and two singlets (6.83, 7.10) which could be assigned to the cyclopropyl hydrogens of the four compounds represented by **31** and **32**.[6,19] The first compound (33%) and the fourth compound (44%) eluted from the vpc were collected and their nmr spectra were taken. The first compound was the *cis*[20] isomer of **31**: nmr (CCl_4), τ 6.83 (1 H, s, HCCl), 4.50 (2 H, m, CH=CH); the fourth was the *cis*[6,18] isomer of **32**: nmr (CCl_4), 6.88 (1 H, t, J = 8.0 Hz, HCCl); no olefinic absorbtion. The second compound eluted from the vpc (10%) and the third (13%) were assigned *trans*-**31** and *trans*-**32** structures, respectively, on the basis of the relative intensities of their cyclopropyl hydrogen peaks in the nmr spectrum of the mixture.

Reaction of Olefin 27 with CH_3Li and CH_2Cl_2.—As above, 10 g of **27** and 12 g of CH_2Cl_2 were treated with 100 ml of 4.6% CH_3Li solution. Distillation of the product gave 4.5 g of a fraction (100–140°, 0.5 mm) which was a mixture of three monoadducts as shown by vpc analysis. The nmr spectrum of the fraction contained two triplets [τ 6.88 (J = 7.5 Hz), 7.30 (J = 3.0 Hz)] and one singlet (6.83) assigned to the cyclopropyl hydrogens of the three compounds represented by **33** and **34**. The first compound (51%) eluted was **33**: nmr (CCl_4), 6.83 (1 H, s, HCCl), 4.57 (4 H, m, CH=CH); the third compound (33%) eluted was *cis* **34**: nmr (CCl_4), 6.88 (1 H, t, J = 7.5 Hz, HCCl), 4.49 (2 H, m, CH=CH). The remaining compound (16%), eluted second, was the *trans* isomer of **34**.

Reaction of Olefin 27 with Dichlorocarbene.—This reaction is reported[21] to give predominately **29**. We find, on repetition the described conditions,[21] that two monoadducts are formed, **29** (85%) and **30** (15%), as determined by vpc analysis and the nmr of **30** which shows peaks at τ 4.43 (2 H, m, CH=CH) and 7.57 (4 H, m, $C{=}CCH_2C{=}C$).

Registry No.—**7**, 18963-03-6; **8**, 18963-04-7; **9**, 18963-05-8; **14**, 18963-06-9; **15**, 18963-07-0; **16**, 18963-08-1; **18**, 18963-09-2; **19**, 18963-10-5; **20**, 18963-45-6; **21**, 18963-46-7; **21**-semicarbazone, 18963-47-8; **22**, 18963-48-9; **25**, 18963-49-0; **25**-semicarbazone, 18963-50-3; **33**, 18963-51-4; **34**, 18963-52-5.

(18) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(19) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

(20) This compound is assigned the *cis* configuration tentatively because its chemical shift is almost identical with the isomeric *cis* isomer **32** which is assigned on firm grounds.[6,19] The hydrogens in both *trans* compounds **31** and **32** are shielded by a double bond, thus chemically shifted to higher field. In addition, one can compare the chemical shift of the similar hydrogens in *cis* and *trans* **34** and **33** with the above compounds and draw the same conclusion: that a hydrogen close to a double bond in these systems is shifted upfield.

(21) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964).